

Determination of Halogenated Aromatic and Polycyclic Aromatic Hydrocarbons Formed During MSW Incineration.

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1. Introduction.

As a consequence of their reported toxicity, considerable attention has been given to the presence of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) in the municipal solid waste (MSW) incineration process. Although interest has centered on PCDDs and PCDFs, other chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) may also be formed during incineration. Recently, reports have appeared on the presence of non-*ortho* and mono-*ortho* substituted polychlorobiphenyls (PCBs) and polychloronaphthalenes (PCNs) during the MSW incineration process¹⁾. However, compared to the literature for PCDDs and PCDFs, reports on the formation of other halogenated PAHs during MSW incineration are limited.

This paper covers the identification and quantification of the major PAHs and halogenated PAHs present in the MSW incineration process.

2. Materials and Methods.

Sampling and extraction procedures for all components were essentially the same as for PCDD and PCDF analysis²⁾ with the addition of a second, back-up XAD-2 sorbent at the end of the sampling train. Sampling was performed at a number of points of a fluidized-bed type MSW incinerator. Additionally, sampling was performed during start-up and shutdown as well as during normal operation.

Depending upon the analyte, GC-MS analysis was performed either on the raw extract or the extract after various clean-up procedures²⁾. Fate of the target analyte during the clean-up procedures was monitored by GC-MS.

The mass spectrometer was operated at both low and high resolution for identification of the components, and at high resolution (>10,000) for quantification. Criteria used for the identification of components were determination of accurate mass, inspection of the isotope ratio, and comparison of mass spectra & GC relative retention times to laboratory synthesised standards.

Analyses for PCDDs, PCDFs, polychlorinated biphenyls (PCBs), polychlorinated benzenes (PCBzs), polychlorinated phenols (PCPhs), polychlorinated naphthalenes (PCNs), and other polychlorinated PAHs were from monochloro- to fully substituted. Commercially available internal standards were used for quantitative analysis of PCDDs, PCDFs, PCBs, PCBzs and PCPhs. Quantitative analysis of

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PCNs was based upon a procedure developed using commercial Halowax as a standard ³⁾, other data are semiquantitative due to lack of appropriate standards.

Total organic halogen (TOX) of the samples was also determined by coulometry.

3. Results and Discussion.

Table 1 shows the halogenated aromatic and polycyclic aromatic hydrocarbons at the baghouse outlet identified by GC-MS analysis, together with their degree of chlorination. The actual total levels (on a nmol/Nm³ basis) of each compound type are given in Figure 1. From this data, it is clear that the major chlorinated aromatic hydrocarbon components, in decreasing order of abundance, are PCPhs > PCBzs > PCNs > PCBs, PCDFs > PCDDs > other chlorinated PAHs. The summed levels of PCPhs, PCBzs, & PCNs account for 98.7% of the total observed halogenated PAHs.

Table 1.

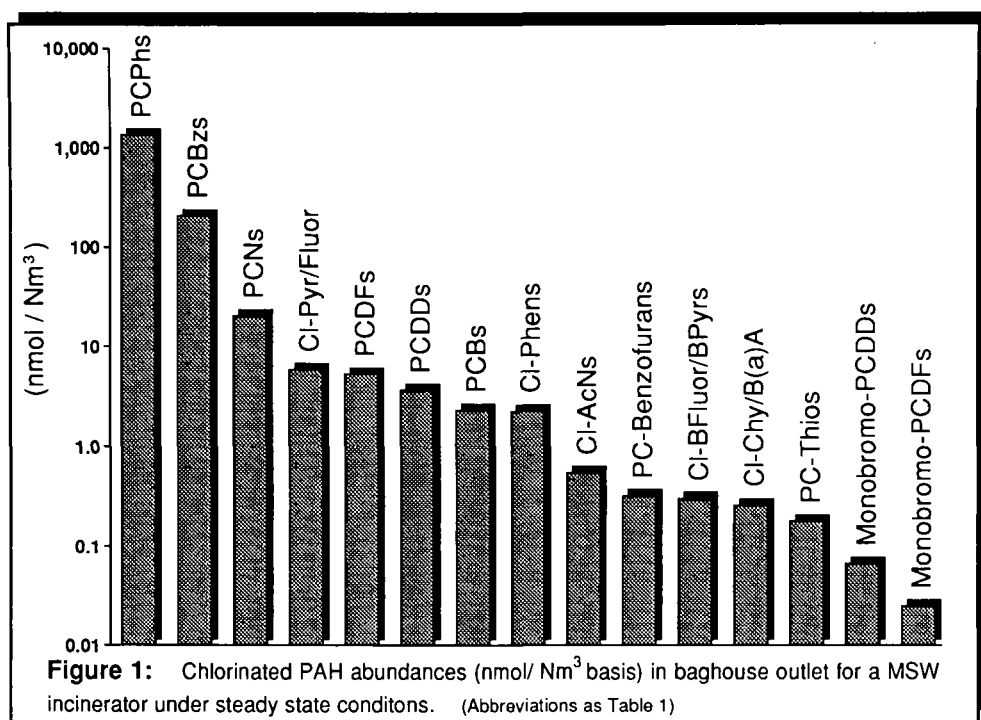
Halogenated aromatic and polycyclic aromatic hydrocarbons identified during MSW incineration.

<u>Component</u>	<u>Range of chlorination observed.</u>
Chlorobenzenes (PCBzs)	1 ⇨ 6
Chlorophenols (PCPhs)	1 ⇨ 5
Chlorostyrenes	1 ⇨ 2
Chlorobenzofurans (PC-Benzofurans)	1 ⇨ 6
Chloronaphthalenes (PCNs)	1 ⇨ 8
Chlorobiphenyls (PCBs)	1 ⇨ 10
Chlorodibenzofurans (PCDFs)	1 ⇨ 8
Chlorodibenzo-p-dioxins (PCDDs)	1 ⇨ 8
Chlorobiphenylenes/acenaphthylenes (Cl-AcNs)	1 ⇨ 8
Chlorophenanthrenes/anthracenes (Cl-Phens)	1 ⇨ 8
Chlorodibenzothiophenes (PC-Thios)	1 ⇨ 8
Chloropyrenes/fluoranthenes (Cl-Pyr/Fluor)	1 ⇨ 7
Chlorochrysenes/benzo(a)anthracenes (Cl-Chr/B(a)A)	1 ⇨ 3
Chlorobenzo(b or j/k)fluoranthenes/benzo(a or e)pyrenes (Cl-BFluor/BPyr)	1 ⇨ 3
Monobromochlorodibenzofurans (Monobromo-PCDFs)	1 ⇨ 6
Monobromochlorodibenzo-p-dioxins (Monobromo-PCDDs)	1 ⇨ 7

The data from the TOX analysis of the samples indicated that the components identified account for most of the chlorinated organic compounds in the sample (Σ Cl-PAHs on Cl basis / TOX value x 100=75~100%).

It should be noted that this data is for one particular incinerator, and data is needed from other incinerators before any general conclusions can be reached on the formation of Cl-PAHs during MSW incineration. Additionally, the sampling procedure used is not designed for very low molecular weight, high volatility compounds. Consequently, determination of the levels of such compounds was considered to be outside the scope of this study.

Figure 2 shows the congener profiles for PCNs, PCBs, PCDFs and PCDDs during start-up, normal

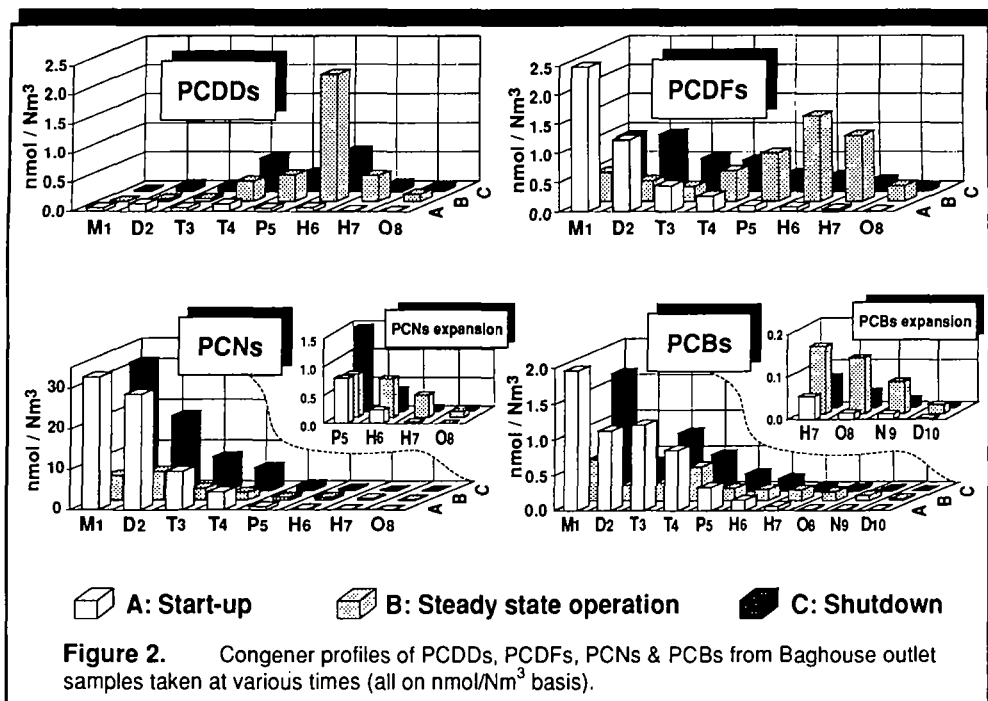


operation, and shutdown. Two points are immediately obvious from this data. Firstly, PCNs, PCBs & PCDFs show a clear trend towards lower chlorinated congeners on start-up and shutdown. In contrast, PCDDs are at a relatively low level for all congeners. Once the MSW incinerator has reached steady state, normal operating conditions, the second clear effect can be seen. The congener profile of both PCDDs and PCDFs shifts to higher levels of chlorination. Also the total level of PCDDs increases significantly. Although there is a slight shift towards higher chlorination levels for PCBs and PCNs, this is not as pronounced as for PCDDs and PCDFs.

The first observation could be due to the lower temperatures observed during start-up and shutdown (~100°C at the baghouse outlet) compared to steady-state operation (~200°C at the baghouse outlet): the lower temperatures favouring the formation of the lower chlorinated congeners. Although data for the baghouse ash (fly-ash) during start-up and shutdown is not available, data from other incinerators have shown an increase in the levels of higher chlorinated PCDDs and PCDFs during start-up and shutdown. This effect has been attributed to the lower temperature prevalent at these times promoting adsorption of the higher chlorinated congeners onto the ash.

The similarity between the congener profiles of PCNs, PCBs and PCDFs at start-up and shutdown may reflect similar modes of formation. Conversely, the low levels of PCDDs at start-up and shutdown, together with the different congener profile, may indicate a different formation mechanism for these components.

Levels of the parent, unsubstituted PAHs were also determined. PCNs, PCBs, Cl-Phens, Cl-Chr/B(a)A, & Cl-Pyr/Fluor all gave ratios of unsubstituted PAH : Σ Cl-PAHs in the range of 50:1 to 5:1. This indicates an excess of the parent, unsubstituted PAH over the combined level for all of the



chlorinated derivatives. However, PCDDs, and to a lesser extent PCDFs, did not fall in this range. Indeed for PCDDs the ratio of unsubstituted dibenzo-*p*-dioxin : ΣPCDDs was less than 0.1. This suggests a relatively lower level of the parent, unsubstituted dibenzo-*p*-dioxin than is seen for the major PAHs observed.

Further work is in progress to investigate these differences in more detail.

4. References.

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